



# Standard Test Method for Monitoring of Atmospheric Corrosion Chambers by Quartz Crystal Microbalances<sup>1</sup>

This standard is issued under the fixed designation B808; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method monitors the reactivity of a gaseous test environment in which metal surfaces (for example, electrical contacts, assembled printed wiring boards, and so forth) and other materials subject to pollutant gas attack undergo accelerated atmospheric corrosion testing. This test method is applicable to the growth of adherent corrosion films whose total corrosion film thickness ranges from a few atomic monolayers to approximately a micrometre.

1.2 The test method provides a dynamic, continuous, in-situ, procedure for monitoring the corrosion rate in corrosion chambers; the uniformity of corrosion chambers; and the corrosion rate on different surfaces. Response time in the order of seconds is possible.

1.3 With the proper samples, the quartz crystal microbalance (QCM) test method can also be used to monitor the weight loss from a surface as a result of the desorption of surface species (that is, reduction of an oxide in a reducing atmosphere). (Alternative names for QCM are quartz crystal oscillator, piezoelectric crystal oscillator, or thin-film evaporation monitor.)

1.4 This test method is not sufficient to specify the corrosion process that may be occurring in a chamber, since a variety of pollutant gases and environments may cause similar weight gains.

1.5 This test method is generally not applicable to test environments in which solid or liquid particles are deposited on the surface of the quartz crystal.

1.6 The values stated in SI units are to be regarded as standard. The values in parentheses are for information only.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to become familiar with all hazards including those identified in the appropriate*

*Material Safety Data Sheet (MSDS) for this product/material as provided by the manufacturer, to establish appropriate safety and health practices, and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

**B810 Test Method for Calibration of Atmospheric Corrosion Test Chambers by Change in Mass of Copper Coupons**

## 3. Summary of Test Method

3.1 A single crystal of quartz has various natural resonant frequencies depending on the crystal's size and shape. The decrease in natural frequency is linearly proportional to the crystal mass and the mass of well-bonded surface films. For crystals with reactive metal films on the surface (usually driving electrodes), the mass of the crystal/metal film increases as the metal oxidizes or forms other compounds with gases adsorbed from the atmosphere.<sup>3,4</sup> Thus, by measuring the rate of resonant frequency change, a rate of corrosion is measured. Non-adherent corrosion films, particles, and droplets yield ambiguous results. A review of theory and applications is given in Lu and Czanderna.<sup>5</sup> See **Appendix X1** for discussion of the quantitative relationship between frequency change and mass change.

3.2 The chamber environmental uniformity and corrosion rate can be measured by placing matching quartz crystals with matching reactive metal films at various locations in the chamber. If the chamber and corrosion rate have been standardized, the corrosion rate on various surface materials that have been deposited on the quartz crystal can be determined.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> King, W. H. Jr., *Analytical Chemistry*, Vol 36, 1964, p. 173.

<sup>4</sup> Karmarkar, K. H. and Guilbault, G. G., *Analytical Chemistry Acta*, Vol 75, 1975, p. 111.

<sup>5</sup> Lu, C. and Czanderna, A. W. Eds., *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, c1984.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee B02 on Nonferrous Metals and Alloys and is the direct responsibility of Subcommittee B02.11 on Electrical Contact Test Methods.

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## 4. Significance and Use

4.1 Corrosion film growth with thicknesses varying from a monolayer of atoms up to 1  $\mu\text{m}$  can readily be measured on a continuous, real-time, in-situ, basis with QCMs.

4.2 The test results obtained for this test method are influenced by various factors, including geometrical effects, temperature, humidity, film thickness, film materials, electrode conditions, gases in the corrosion chamber, atmospheric pressure, and so forth. Calibration of coated crystals and instrumentation and reproducible crystal operating conditions are necessary for consistent results.

## 5. Apparatus

5.1 Apparatus can be a simple series circuit of crystal (with electrodes and sensing film), oscillator (typically 6 MHz) and frequency counter ( $\pm 10$ -Hz accuracy and stability), as schematically shown in Fig. 1.

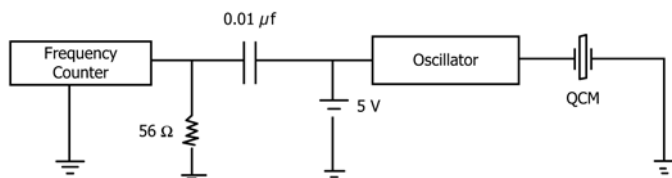


FIG. 1 Schematic of QCM and Related Electronics

5.2 *Commercial, Thin-Film Monitors*,<sup>6</sup> incorporating those functions that read out thicknesses or weight gain are also available and acceptable after they have been calibrated.

5.3 *Microbalance*, with an accuracy of  $\pm 2 \mu\text{g}$  is needed for calibration procedures.

5.4 *Recording Devices or Computers* are needed for real-time, continuous measurements.<sup>7</sup>

## 6. Materials

6.1 Crystals shall be of the AT<sup>5</sup> cut variety with a resonant frequency in the MHz range and matched to the frequency measuring apparatus used. Quartz crystal surfaces shall be polished to a surface finish with an arithmetical mean deviation,  $R_a$ , of less than 0.1  $\mu\text{m}$ . With this surface finish, the crystal appears optically transparent to the human eye.<sup>8</sup>

6.2 Electrodes, used to drive the crystal's resonant frequency, can be made from any electrically conducting material and usually are a metal film evaporated on the quartz crystal surface. The material under study or being used to calibrate the system may be the same as or different than the electrode material. If the two materials are different, the potential corrosion of the electrodes shall be accounted for during the design and subsequent experiments. Depending on the materials under test, the QCMs can have copper, silver,

nickel, zinc, gold, etc. electrodes. The preferred method of deposition is by evaporation for a high purity, smooth surface. If sublayers are used to enhance the adhesion of the final electrode, they should be covered by the final electrode material so that less than 1 % of the metallic area is of exposed sublayer material. Because of the fragility of the metal electrode there should be multiple (three or more), spring-loaded contacts between the crystal and electronics.

6.3 After metallization of the crystals, they should be stored in desiccators. After two years storage or if the metallization shows discoloration or staining, the crystals shall be discarded. Crystal surfaces should not be chemically or mechanically cleaned before use in the corrosion chamber. They should be blown clean with inert compressed gas. Chilling and condensation on the surface, as can occur with the use of pressurized fluorocarbons, shall be avoided. Care shall be exercised so that the crystals are only handled by clean tweezers or tongs and never touched by hands.

## 7. Calibration

7.1 QCMs and its electronics shall be calibrated initially in a given corrosion system and thereafter on an annual basis. Calibration shall be performed with the same shape and size of crystal holder to be used during operation. Recalibration shall be performed if the crystal holder geometry is changed. Calibration can be done by comparison to a standard such as actual gravimetric weighing on a microbalance ( $\pm 2 \mu\text{g}$ ). Use a sample of the same material as the sensing film with a minimum area of 5  $\text{cm}^2$  and a thickness of 0.1 to 0.6 mm (see Test Method B810). Foil surface roughness should be within  $\pm 20$  % of the QCM sensing film roughness. The procedure for the generation (that is, evaporation) and cleaning of the gravimetric sample should be the same as used for the sensing films. The age and storage of the gravimetric sample should be comparable to the age of the QCM sensing film. Allow the foil to equilibrate with the microbalance atmosphere for 0.5 h, then weigh the sample with  $\pm 2 \mu\text{g}$  accuracy before exposure. Suspend the weighed gravimetric sample between two similarly treated QCMs spaced 20 cm apart with the large surface area dimension of the samples parallel to the air flow. After sufficient exposure, as determined in the paragraph below, remove the sample from the corrosion chamber, equilibrate it with the balance atmosphere, and reweigh. The gravimetrically measured, foil weight gain per unit area should be within  $\pm 10$  % of the calculated weight gain, found on the active area of the QCM.

7.2 A weight gain of the metal foil of 50  $\mu\text{g}$  is sufficient for a microbalance with  $\pm 2 \mu\text{g}$  reproducibility and is sufficient for calibration. (If the reproducibility of the microbalance is poorer than  $\pm 2 \mu\text{g}$ , proportionally greater weight gain shall be used.) If the sensing material was copper and the corrosion film was  $\text{Cu}_2\text{O}$ , 50  $\mu\text{g}/5 \text{ cm}^2$  would correspond to a film thickness of 149 nm if the density of  $\text{Cu}_2\text{O}$  was 6  $\text{g}/\text{cm}^3$  and the percentage of oxygen in the film was 11 % (16/143). For improved accuracy, greater weight gain may be used. However, the calculated thickness of the corrosion film should not exceed 50 % of the electrode thickness.

<sup>6</sup> Instruments of this type are used in semiconductor manufacture and may be found by searching for deposition thickness monitors.

<sup>7</sup> Schubert, R. "A Second Generation Accelerated Atmospheric Corrosion Chamber," *ASTM STP 965*, 1988, p. 374.

<sup>8</sup> Most instrument suppliers of thin film monitors also sell crystals with various coatings and roughness.

## 8. Procedure

8.1 All metal surfaces that are not being used in the measurement should be shrouded or coated with a nonreactive material to protect the surfaces from unwanted corrosion (that is, clear nail polish, Q-dope, heat shrink TFE-fluorocarbon, and so forth). It is especially important to protect any electrical connections that are being used for measurements or providing power from the corrosive atmosphere under investigation.

8.2 Do not handle the crystals by hand or with anything that leaves a residue after evaporation on the crystal electrodes. Use caution in all handling to avoid scratching the sensing film surface.

8.3 One QCM with a sensing film inert to the test environment should be in the system to monitor changes in the amount of relative humidity in the system, adsorbed hydrocarbons, and so forth. (A gold-coated QCM is usually a good choice for this application.) At the end of the chamber exposure when all the pollutant gases have been removed and the humidity has been returned to its initial value, the frequency of this QCM should still be at its initial value. (This is not meant to replace a relative humidity meter, rather it verifies the system electronics stability.)

8.4 For determining the chamber's spatial uniformity of pollutant gas, QCMs should be located uniformly at various locations around a chamber to confirm that the corrosion rate is the same ( $\pm 10\%$ ) at all locations. A typical distribution is one sensor per every 7 L of volume or 4 sensors/ft<sup>3</sup> for a cubic chamber of 28-L (1-ft<sup>3</sup>) volume. See Test Method B810 for typical distribution schemes of QCM. This density can be increased or decreased depending on the chamber shape, chamber loading, and chamber airflow.

8.5 It is preferable that the monitoring QCMs shall be oriented with the sensing surface perpendicular to and facing

the air flow. If another orientation to the air flow is used, the monitors orientation relative to the air flow shall be reported in the test report.

## 9. Report

9.1 Recorded data should include the following:

9.1.1 Types and concentrations of the corrosive gases in the corrosion chamber, relative humidity, temperature, and air flow characteristics (for example, direction, velocity, turbulence, and exchange rate).

9.1.2 Sensing material(s), weight gain(s), versus time and date for the QCMs, and their location in the chamber.

9.1.3 Description of the samples in the chamber during the experiments, including the material, surface area, and location in the chamber.

## 10. Precision and Bias

10.1 *Precision*—The precision of this test method has been determined to be  $\pm 10\%$  using copper QCMs. This experiment is reported in the open literature.<sup>9</sup> However, as a result of variations in fixturing, film composition, film smoothness, and air flow characteristics, all QCM measurements should be compared to total corrosion rates as determined by Test Method B810 and described previously.

10.2 *Bias*—Crystal fixturing may produce large variability in chamber-to-chamber results. Since there is no acceptable reference suitable for determining the bias for QCMs, bias has not been determined.

## 11. Keywords

11.1 corrosion monitor; piezoelectric crystals, sensors, thin-film monitor

<sup>9</sup> Schubert, R. and Neuburger, G. G., *Journal of the Electrochemical Society*, Vol 137, No. 4, 1990, p. 1048.

## APPENDIX

### (Nonmandatory Information)

#### X1. SAUERBREY EQUATION RELATING FREQUENCY CHANGE OF A QUARTZ CRYSTAL MICROBALANCE (QCM) TO MASS CHANGE IN AN ATMOSPHERIC CORROSION TEST

X1.1 A piezoelectric quartz crystal utilizes the Converse Piezoelectric Effect to determine mass changes as a result of frequency change of the crystal. Material such as copper is coated onto the crystal that bonds with a material from the atmosphere. When the gaseous material bonds to the material on the crystal surface, its added mass lowers the crystal frequency. The Sauerbrey equation<sup>10</sup> relates the frequency change to the mass change. One form of the Sauerbrey equation is given as follows:

$$\Delta f = -\Delta m_d f^2 / r_q v_q \quad (\text{X1.1})$$

where:

$\Delta f$  = change in frequency of the crystal,  
 $\Delta m_d$  = change in mass surface density ( $m_d$ , mass per unit of surface area),  
 $f^2$  = square of the frequency of the crystal,  
 $r_q$  = density of quartz ( $2650 \text{ kg m}^{-3}$ ), and  
 $v_q$  = velocity of propagation of sound in quartz ( $3340 \text{ m s}^{-1}$ ).

X1.1.1 For small changes in mass of the crystal and related small changes in frequency, the relation:

$$\Delta f = -K \Delta m_d \quad (\text{X1.2})$$

is adequate for purposes of this test method where K incorporates the square of the initial frequency and the material constants. Since a frequency change of one part in  $10^7$  is

<sup>10</sup> Sauerbrey, G. Z., *Z. Phys.*, 1959, 133, 206.

readily detected with common instrumentation, when one calculates the related change in mass one finds that a mass increase in the nanogram range is detectable. If one determines the area of the crystal that corrodes and assumes a uniform film over that area, an estimated film thickness can be calculated from the mass change and handbook values of the density of

the compound in the corrosion film. The composition of the film may be inferred from the chemistry of the atmosphere or determined by chemical analysis. If analysis of the corrosion film indicates a mixed film, it is still possible to estimate the thickness of the film using proportions of compounds and their densities.

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